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Review Article

Role of Thermosetting Polymer in Structural Composite

Ayesha Kausar[1]

[1] Nanoscience and Technology Department, National Center For Physics, Quaid-i-Azam University Campus, Islamabad, Pakistan

Abstract

Thermosetting resins are network forming polymers with highly crosslinked structure. In this review article, thermoset of epoxy, unsaturated polyester resin, phenolic, melamine, and polyurethane resin have been conversed. Thermosets usually have outstanding tensile strength, impact strength, and glass transition temperature (T_g). Epoxy is the most widely explored class of thermosetting resins. Owing to high stiffness and strength, chemical resistance, good dielectric behavior, corrosion resistance, low shrinkage during curing, and good thermal features, epoxy form the most important class of thermosetting resins for several engineering applications. Here, essential features of imperative thermosetting resins have been discussed such as mechanical, thermal, and non-flammability. At the end, employment of thermosetting resins in technical applications like sporting goods, adhesives, printed circuit board, and aerospace have been included.

Keywords: Thermoset; epoxy; mechanical; non-flammability; application

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***Correspondence to:** Ayesha Kausar, Nanoscience and Technology Department, National Center For Physics, Quaid-i-Azam University Campus, Islamabad, Pakistan

E-mail: asheesgreat@yahoo.com

1. Introduction

Highly cross-linked thermosetting polymers mainly epoxy resins and unsaturated polyesters are significant class of synthetic material. The chief difference from other polymers are due to their compactly crosslinked structure. The high crosslinking may lead to number of outstanding superior features mainly such as glass transition temperature, high specific structure and strength, high creep resistance, good dimensional stability at high temperature, and good solvent resistance [1]. These features, in conjunction with ease of processing, have directed extensive employment of thermosetting polymers as encapsulating constituent, tooling compounds, electronic substrate, and packaging. Thermoset polymers are perhaps the most significantly as matrix material for strengthened composites [2]. Unfortunately, high crosslinking degree in thermosetting polymers makes them intrinsically brittle with poor resistance to crack initiation and propagation. Thus, the lack of toughness influences the potential of highly crosslinked thermosets in technical applications. For example, primary damage initiation occur in fiber reinforced laminated composites due to lack of toughness with matrix cracking and delamination. Consequently, enhancement in fracture toughness of thermosetting polymers may lead to great improvement *via* increasing damage initiation threshold and long term consistency of fiber-reinforced composite [3]. Thermoset composite constituents are employed in extensive range of applications in industries such as automotive and constructions. Thermosets have been fabricated in various types. For more demanding employment, continuous carbon fibers and epoxy resins are utilized for critical applications in automotive, aircraft, and aerospace industry. Accordingly, thermosetting polymers have outstanding thermal, mechanical, and electrical features. Due to these properties, thermosets have been used almost in every field and in every application.

2. Thermoset polymer

The network forming polymers are called thermosets. These polymers consist of epoxy, unsaturated polyester, phenolic, dicyanate, polyurethane, acrylate, bismaleimide, and many other polymers [4, 5]. The structures of some thermoset polymers are shown in Fig 1.

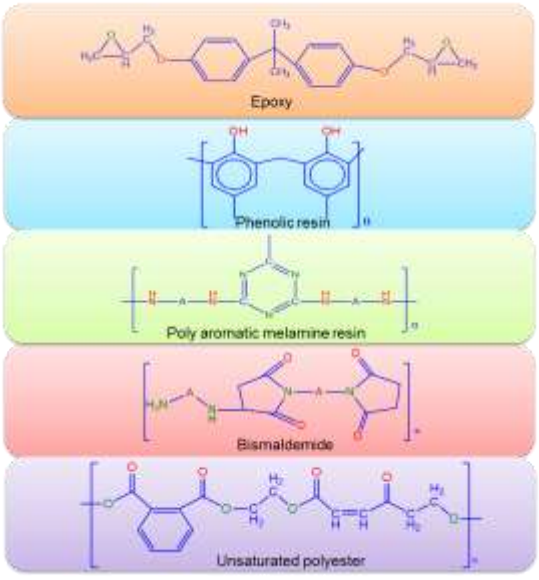


Fig. 1 Different types of thermosetting resins.

In comparison to that of thermoplastics, there is an involvement of chemical reaction during their use. As a result of these reactions, there is an increase in viscosity of the materials. Consequently, polymer may become crosslinked and sets. The degree of cross linking in thermoset polymers is shown in Fig 2. These polymers no longer dissolve or flow. Most often thermally activated cure is called thermoset, nonetheless there are conditions under which network is formed in material. Light activated curing is also supposed to form thermoset. Some thermosetting adhesives are crosslinked by dual cure mechanism i.e. by either light or heat [6, 7]. Thermosets, are mixtures of small repeating units, often called monomers in the uncured state. Catalysts are generally added to speed up the reaction. Most of the thermoset integrate the particular fiber or filler strengthening for cost reduction and for modification of physical feature, reduction of shrinkage during cure, and for enhancement of flame retardancy [8].

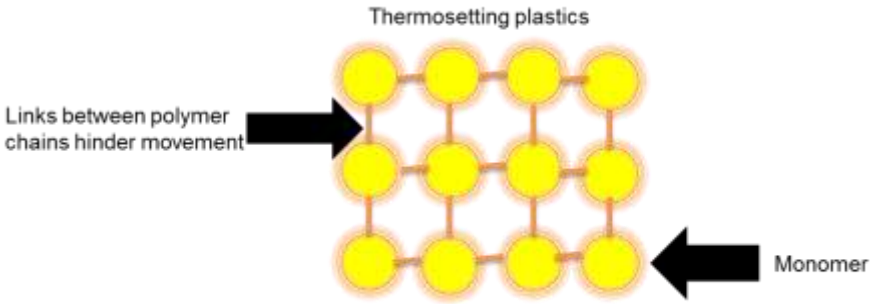


Fig. 2 Crosslinking degree in thermoset polymers.

3. Types of thermosetting polymer

Thermosets, because of irreversible curing reaction, are rigid and three dimensional crosslinked plastics. The soluble and fusible starting material may integrate numerous filler such as glass, minerals, fibers, and glass mate. As a result of the three dimensional crosslinked structure, thermoset do not flow even on heating. The main types of thermoset resins are epoxy resins, urea, melamine resins, unsaturated polyester resin, phenolic, and polyurethane resins [9, 10]. Thermosets generally comprises of good dimensional stability, chemical resistance, thermal stability, and electrical features. Due to these properties, thermoset found great employment in numerous applications mainly primary and secondary structural parts in aerospace, adhesives, floor and counter tops for manufacturing facilities and homes, conductive polymer elements, printed circuit board, dental material, encapsulating material for electronic applications, and recreational products i.e. bicycle frames, tennis racquets, golf club, and fishing rods [11].

3.1. Epoxy

In the manufacture and characterization of engineering materials, there exist significant opportunities and challenges. In engineering applications, there is an increase in the use of polymeric materials due to low cost, ease of manufacture and processing, low weight, and good chemical properties. After the advent of structural adhesives, several recent technological achievements have become possible. Polymers with high chemical and corrosion resistance, good mechanical and thermal properties, low shrinkage upon cure, outstanding adhesion to various substrates, and good electrical insulating

properties are known as epoxies. They are usually brittle and temperature sensitive in terms of structural applications. Epoxy is characterized by a three membered ring known as epoxy/oxirane/epoxide or ethoxyline group. Prepolymer, with more than one epoxide group, having low molecular weight, is called epoxy resin. Epoxy resin was initially discovered by Prileschajew in 1909 [12].

3.2. Phenolic resin

Phenolic resins (PR) have been extensively used as adhesives, coatings and composites because of their outstanding flame resistance, insulativity, heat and chemical resistance, and dimensional stability. Moreover, their applications has significantly limited by inherent brittleness. Materials utilized as toughening agents of PR consists of elastomers such as natural rubber and nitrile butadiene rubber (NBR), reactive liquid polymers such as liquid nitrile butadiene and carboxyl terminated butadiene acrylonitrile, and plastics such as polysulphones and polyamides [13, 14]. The most widely employed toughening agents are elastomers because of their low cost and high efficiency. Moreover, the phenolic network is subjected to deterioration in heat resistance, strength and modulus after integration with elastomers and flexible compounds. For the enhancement of heat resistance, stiff aromatic heterocyclic structures are generally introduced into PR molecules [15].

3.3. Unsaturated polyester

The recent invention related to that of unsaturated polyester resin is utilization in manufacturing of structural parts containing itaconate ester monomers as reactive unsaturation. These ester monomers are generally suitable for high temperature applications in which important factor are high thermal stability. The meaning of high temperature applications is that they are capable at temperatures above 750 ℃. From ecological point of view, there is great desire for making unsaturated polyesters for manufacturing of structural parts. The employment of petroleum based monomers in the production of consumer products is expected to decrease in coming years due to continuous increase in oil price and high rate of known oil reserves depletion. This is linked with the strict government regulations all around the world regarding environmental protection against pollution. Renewable resources are explored as possible alternative to petroleum based monomers. With the decline in limited petroleum resources, use of renewable resources as chemicals for industrial applications is of great interest. An appropriate example of biobased building block for unsaturated polyesters is itaconic anhydride [16].

3.4. Polyurethane resin

Polyurethane (PU) is an extremely useful polymeric constituent which is widely employed in automobiles, construction, and biomaterials. Polyurethane is synthesized by the reaction of diisocyanate and polyester-based diol followed by the reaction with chain extenders to form macromolecules. Therefore, the studies highlighting the development of technologies and flame retardant materials have been increased over many years [17]. Recently, halogen free flame retardants such as organophosphate compounds have been employed in polymeric constituents to inhibit the generation of eroding halogenated gases as well as discharge of supposed endocrine disrupting chemicals during combustion. It was believed by the most of researchers that the efficiency of phosphorus flame retardant is chiefly because of condensed-phase retardation. Thermal decomposition

of phosphorus constituent may occurr earlier (~30 ℃) in comparison to that of phosphorus-free polyurethanes [18].

4. Imperative features of thermoset polymer

Thermoset polymers are matrix for choice for fiber reinforced composites employed in diverse variety of applications such as aerospace. They have high strength, stiffness, as well as thermal and creep resistance in comparison to that of thermoplastic polymers. There features not only depend on their composition or chemistry, but also on their molecular structure, degree of polymerization, and molecular structure [19]. It has been considered that, in comparison to thermoplastics, thermosets are stiffer or thermoplastics are harder than thermosets. However, such considerations are derived from generalization of rubbery state features in which crosslinking density plays an important role. For instance, polystyrene (PS) is stiffer and brittle than majority of epoxy network of DGEBA (diglycidyl ether of bisphenol-A) type epoxy crosslinked by diamine hardener with glass transition temperature greater than that of PS (~380 K) [20, 21]. The polymerization of monomer reactant (PMR) type polyimides is thermosetting polymers that comprise outstanding processability, thermal stability, and mechanical features. These constituents are fascinating for employment in aerospace components where reliability and durability are of critical concern. Among material requirements for these applications are outstanding glass transition temperature (T_g), high temperature stability in various environment, and good mechanical features over wide range of temperature [22].

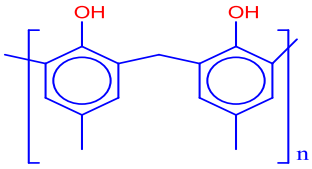
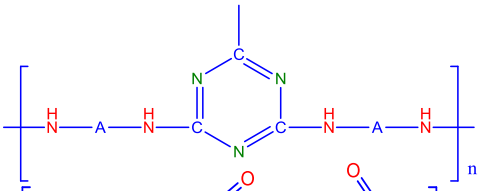
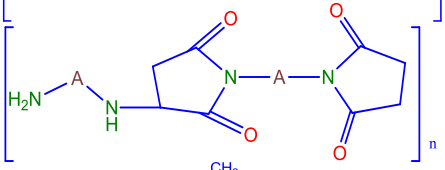
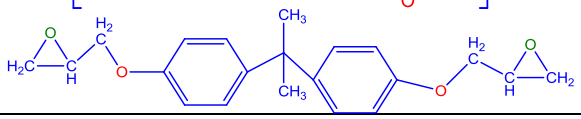
4.1. Mechanical properties

Epoxy based composites, because of their two component implementation, are suitable elements for changing the characteristics of end product following a quasi-infinite variety. Fore example, the glass transition temperature of epoxy amine network can be greatly adjusted between -15 to 220 ℃ as a function of diamine used in formulations. Consequently, these materials are present in wide range of applications mainly printed wiring circuit boards, adhesives, heavy duty and powder coatings, aerospace, automotive and aircraft applications, and so on. Rubber modified epoxies are widely demarcated in literature [23]. The main purpose of the system is to strengthen the brittle epoxide network with rubbery dispersed phase. Among them the reactive liquid rubbers like CTBN (Carboxyl-terminated butadiene acrylonitrile) are the most popular [24]. Significant toughness improvement at low loading level, while decreasing the influence on other important features, has been the major issue. As the considered materials are heterogeneous, this may be obtained through a careful control of phase separation and morphologies [25, 26]. Unsaturated polyester resins (PER) have been widely utilized as matrix for glass fiber reinforced composites and bulk and sheet molding composites because of their low manufacturing costs and high tensile strength. Moreover, major drawback of PER (such as their inherent brittleness, polymerization shrinkage and low resistance propagation because of their degree of crosslinking) have restricted the applications to the situations where the stress is relatively low and preferably static. Thus, PER modification is necessary to fulfill the industrial demands [27]. The inclusion of low profile additives mainly poly(vinyl acetate) (PVAc) and poly (methyl methacrylate) in PER may overcome the high polymerization shrinkage during copolymerization of unsaturated polyester resin with crosslinking monomer [28, 29].

4.2. Thermal properties

Curing temperature and time play a significant role in determination of the network topology as well as degree of conversion. There have been several experimental studies for the characterization of influence of conversion degree on material features of thermoset polymers. Among the properties studied, the most extensive characteristic is glass transition characterized of DGEBA/Tetramethylammonium Borohydride (TMAB) and dicyanate ester/polycyanurate toughened epoxy resin [30, 31]. A common trend of all the studies is that an increase in T_g was observed with increasing conversion in non-linear fashion with increasing dependency for high conversion degree. Influence of atomistic stimulation on conversion degree of T_g was also observed [32, 33]. The Tg of different thermoset polymers is shown in Table 1.

Table 1 Glass transition temperatures of some thermoset resin.

Polymer	Polymer structure	T_g (℃)
Phenolic		525
Poly aromatic melamine		450
Bismaleimide		425
Epoxy		335

In biological systems inspired by phenomenon of self-healing, the synthesis of man-made self-healing polymeric constituent has become novel paradigm and fascinating area of research. Self-healing of constituent has ability of repairing or recovering themselves during mechanical and thermally induced damage. Self-healing can be activated by external stimulus or can occur autonomously once a multiple times [34]. The valuable features may increase the lifetime use of numerous polymeric products. Moreover, complex and costly synthetic routes and loss of mechanical features after self-healing or remending has restricted their further progress. The Diels-Alder (DA) reaction and its Retro-Diels-Alder (RDA) analogue represented highly interesting route for the introduction self-healing features polymeric system. Thus, all of the thermosetting resins have outstanding features [35, 36].

4.3. Non-flammability properties

Epoxy resins are broadly applied as advanced composites matrices in electrical/electronic industries, where a capable flame retardant grade is needed. However, the major drawback of these constituents is fire risk. Two main routes to obtain flame retardancy of polymers are generally known as the reaction and the addition route. The former is given much attention currently [37]. Traditionally with the epoxy resins,

brominated reactive compounds have been utilized as co-monomers for the achievement of flame retardancy [3]. Although, flame retardant epoxy resin comprising bromine may produce corrosive and obscuring smoke. Consequently, they may give rise to supertoxic halogenated dibenzodioxins and dibenzofurans with injurious influence on human health and environment. Presently, in consideration of environmental problems, research on halogen-free fire retardant epoxy resins have gained great deal of interest [39, 40]. One of the most effective routes to deliberate flame retardancy of epoxy resin is phosphorylation. While phosphate based epoxy resins also comprise outstanding flame retardancy by employing amine curing agents. By the additions of phosphorus and nitrogen flame retardant, significant improvement have been observed in flame retardancy of epoxy. The limiting oxygen index (LOI) has been measured according to ASTM D-2863. It is often employed to illustrate the relative flammability of numerous polymers and within the constraints of LOI test. It has been explored that the polymer with greater LOI have lower flammability than a polymer with lower LOI [41, 42]. LOI values of some generally employed polymers are shown in Table 2. From the LOI values, polyvinyl chloride (PVC) with LOI values of 23-45 has appeared to be appropriate for employment as polymer matrix from flammability point of view. However, PVC has produced corrosive hydrogen chloride gas and heavy smoke during burning. It has been used as matrix material of composites for end use in aircraft and ships [43, 44]. The diagram of schematic gasification is shown in Fig 3 and the fire resistance of thermoplastic and thermoset polymers is shown in Table 3.

Table 2 LOI of thermosetting polymer.

Polymer	LOI (vol.%)
Polypropylene	17
Polyethylene	17
Polybutylene terpthalate	18
Polystyrene	18
Vinyl ester	20-23
Polyamide (Nylon 6,6)	21-30
Polyethyene terpthalate	21-33
Polyamide (Nylon 6)	21-34
Epoxy	23-27
Polyvinyl chloride	23-45
Polyamide (Nylon 11)	25-32
Phenolic	25-57
Acrylonitrile butadiene styrene	31-35

Table 3 Relative fire resistance of polymer.

Thermoplastic	Thermoset	Fire resistance
Acrylonitrile butadiene styrene	Epoxy	Low
Polyaryl sulfone	Poly aromatic melamine	
Polyether sulfone	Phenolic	
9,9-Bis-(4-hydroxy phenol (flourine)		High
polycarbonate-poly(dimethyl siloxane)		

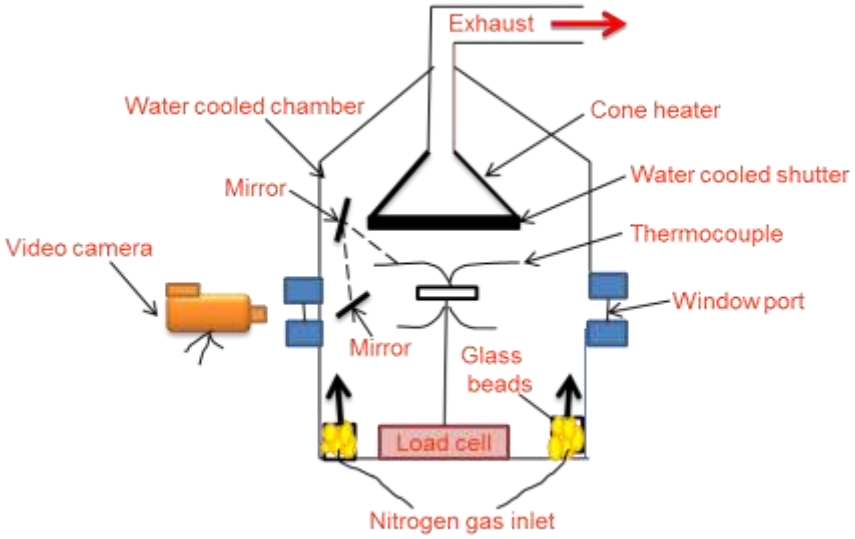


Fig. 3 Gasification apparatus.

5. Application

The progress of advanced composites have led to ever growing employment in aerospace, electronics, defense, automotive, and other technical industries due to inherently outstanding specific modulus and strength. Epoxy resins deliver excellent adhesion, chemical resistance, corrosion, and toughness. In a range of markets, thermosets are found comprising transportation, construction, industry, electronics, and packaging, protective coatings, adhesives, fiber-reinforced forms, and as structural materials [45-51]. In 2009, Global construction of epoxy resins was about 1,800,000 MT. The largest markets of epoxy is in coatings and electronics, which report for nearly 80% of all epoxy resin use. Composites represent a slight use of epoxy resins [52, 53]. The shape memory polymer (SMP) is type of macromolecular smart constituent that can give response to external stimulus by the change in it macroscopic features mainly color and shape. Its original shape is recovered from the temporary shape. Additionally, SMP have great significance of being inexpensive, light weight, low density, high shape of deformability, good manufacturability, good biodegradability, and easily tailorable glass transition temperature in comparison to that of shape memory alloys and shape memory ceramics [54]. Thus, growing number of international researches have been focused on the development of shape memory influence in polymers since 1980s. Nowadays, much of the research is devoted to SMP application in aerospace. Moreover, space environment is enormously harsh and various significant features must be considered during selection of structure constituents in space environment mainly ultra-high or low temperature cycle effect, high vacuum, ultraviolet (UV) radiation, and so on [55, 56]. The typical thermomechanical cycle processing of SMP under compression testing is shown in Fig. 4.

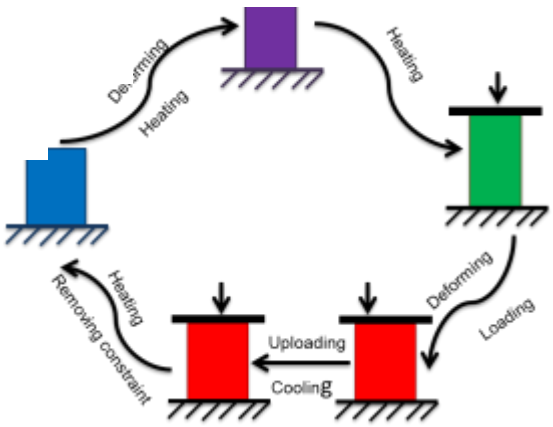


Fig. 4 Typical thermo-mechanical cycle processing under compression testing.

6. Conclusion

In this review article, significance of thermosetting polymers has been stressed. It was studied that the thermosetting polymers form important class of engineering polymers. To explore the full potential of thermosets, thermal, mechanical, and flammability properties of these polymers have been overviewed. Different types of thermosetting resins have also been conversed and their features were compared. According to literature, thermosets have outstanding glass transition temperature, thermal decomposition temperature, mechanical strength, and non-flammability characteristics. Essential applications of thermosetting resin focus aerospace, aircraft, construction, and electronic industries.

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